

PATENT SPECIFICATION

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(72) Inventor PHILLIP E. SOKO



(54) COSMETIC COMPOSITION

(71) We, THE GILLETTE COMPANY, a corporation organized and existing under the laws of the State of Delaware, United States of America, of Prudential Tower Building, Boston, State of Massachusetts, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to cosmetic compositions for conditioning hair, and more specifically to such cosmetic compositions containing high molecular weight water soluble polymers having a multiplicity of quaternary salt groups.

Modern day living results in exposure of individuals to increasing amounts of sunlight, chlorine water, harsh detergents and chemical specialty products. Because of this, cosmetic and toiletry products must be capable of leaving the hair with lustre and softness while overcoming natural or induced harshness and dryness. This is in addition to a product's primary purpose whether it be to impart or maintain a hair style, or to alter the natural colour of the hair. There is, in each case, the corollary requirement that the hair be left with an improved appearance and feel. In those types of products where the human being is subjected to chemical reaction, it is important that the cosmetic be capable of restoring the hair as nearly as possible to its original state. In any case, the user of cosmetics or toiletries judges the state or condition in relation to the feel of the hair, and frequently by its ease of combing.

There have been in the past several means of achieving this end. One of the simplest means of doing so has been to dissolve a conditioning material in the cosmetic or toiletry product. In some cosmetic forms, after application, the evaporation of solvent deposits the conditioning material. This method has been useful in the deposition of natural gums, certain of the synthetic poly-

mers, and a few protein derivatives. A shortcoming of such systems, when aqueous, is that any such material that can be dissolved in water is equally subject to subsequent removal by simple washing. Water insoluble materials deposited on hair from organic solvent, while more resistant to water removal, require that the hair be subjected to the action of organic solvent materials capable themselves of extracting natural constituents of hair. Non-aqueous oleaginous mixtures have sometimes been used to deposit coatings of conditioning materials on hair. The standard hot oil treatment for hair and some hair grooms are representative. Such oil coatings, however, whether of mineral, animal or vegetable origin, are generally too greasy to satisfy modern tastes. Application of conditioning materials to hair from emulsion systems is often practiced enabling many materials to be used which would otherwise be difficult to apply. As in the previously indicated case of application from aqueous solvent systems, the deposited film is generally easily removable by simple water washing, the original emulsifying materials present in the composition also remaining behind to reduce the binding potential of the conditioning material to hair.

One of the more interesting and most widely used means for overcoming a harsh feeling in human hair is by the deposition of cationic materials which are absorbed by the protein structure of the substrate. Especially useful have been the cationic fatty quaternary compounds having fatty chain lengths of approximately 8 to 18 carbon atoms. These materials which form the basis of many of the conditioning hair rinse products found on the market, though substantive to hair, cannot withstand, to any substantial extent, the action of most detergent materials used for personal cleansing. While these materials are an improvement over the older modes of conditioning described above, they can soften the hair excessively leaving it unmanageable and with a lack of

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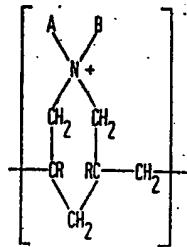
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body. It has not generally been found helpful to simply reduce the concentration of the quaternary material since to do so would reduce the combing benefits and/or conditioning properties imparted by such products to the hair. Furthermore, because many of the most widely used products for treating hair contain anionic surfactants and because cationic materials are usually inactivated by reaction with anionic surfactants, it is customary to employ cationic materials only as a separate composition such as a post shampoo rinse separately applied. There has been disclosed another means of depositing conditioning materials on hair. U.S. Patent No. 3,313,734 and Canadian Patent No. 762,893 describe cosmetic compositions containing certain polymers having cationic sites. The compositions yield a fine precipitate of the polymer components upon dilution with water. This precipitate adheres to the surface of the hair shaft, thereby altering surface properties of the hair fibres. This effect, as described in the above patents, is limited, however, to shampoo compositions and produces in many instances an undesirably heavy deposit of material which leaves the hair feeling coated and unclean.

We have now discovered that the surface characteristics of hair can be modified and its condition improved by applying thereto a composition containing certain water soluble polymers containing quaternary groups.

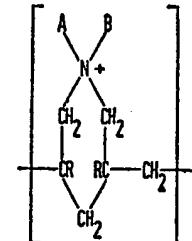
According to the invention, there is provided a cosmetic composition for application to hair, comprising a cosmetic base (as herein defined) and a high molecular weight water soluble quaternary ammonium polymer having a molecular chain containing units of the formula:



wherein R is hydrogen or methyl and A and B are independently alkyl groups having from one to twenty-two carbon atoms, lower hydroxyalkyl groups, or lower alkyl groups containing terminal amido groups, or wherein A and B taken together with N are piperidinyl or morpholinyl groups.

The invention further comprises a process of changing the surface characteristics of hair, which comprises applying thereto a cosmetic base (as herein defined) and a high molecular weight water soluble quaternary

ammonium polymer having a molecular chain containing units of the formula:



wherein R is hydrogen or methyl and A and B are independently alkyl groups having from one to twenty-two carbon atoms, lower hydroxyalkyl groups, or lower alkyl groups containing terminal amido groups, or wherein A and B taken together with N are piperidinyl or morpholinyl groups, the cosmetic base and the polymer being applied together or in sequence.

By "cosmetic base" we mean (1) a hair waving or straightening lotion comprising a keratin reducing agent, or a neutralizer therefor containing an oxidizing agent or (2) a hair bleaching composition comprising an oxidizing agent or (3) a hair dye composition comprising an oxidative or non-oxidative dye.

Any of the usual cosmetic adjuvants may be employed in the cosmetic bases employed in the present invention, and they may be packaged in pressure containers along with conventional propellant liquids for convenient dispensing.

The polymers are equally effective when an anionic surface active agent is present in the cosmetic base as when only cationic, nonionic, or ampholytic agents are present despite the fact that ionic interaction would be expected to lead to the formation of an inactive and insoluble catan wax. The polymer can be used effectively in amounts ranging upwardly from 0.05% by weight of the cosmetic base. There is no critical upper limit to the amount of polymer which may be present, and amounts as great as 40% by weight of the cosmetic base or even more may be used, particularly when application of the composition to the hair is followed by a water rinse. If the composition is supplied in such concentrated form, however, it is generally desirable to dilute it with water to a polymer content of 0.5 to 15% by weight before use. The polymers are also effective when employed in non-aqueous compositions, for example alcoholic compositions, but aqueous compositions are preferred because of their lack of tendency to extract desirable components from the hair. The cosmetic bases in which the polymers may be effec-

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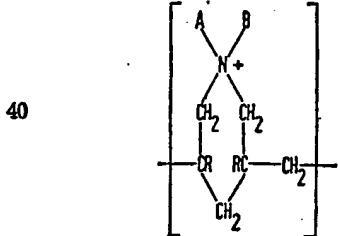
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tively employed may vary widely in acid or base content, having a pH, when in water, from 1.5 to 11.5. The polymers are effective to alter the surface characteristics of the hair and maintain the desired conditioned effect even though the application of the cosmetic base is followed, intentionally or unintentionally, by a water rinse. Indeed, the conditioning effect produced by incorporating these polymers in a cosmetic base is remarkably durable, persisting in many cases through several successive rinses and even through successive washings with a conventional detergent or shampoo composition. In fact, most cosmetic bases contain from 0.5 to 20% by weight of a surface active agent which in itself would be expected to remove the polymer even if no shampoo were subsequently used.

Particularly important and useful embodiments of the present invention are hair straightening and hair waving compositions, which contain reducing agents such as sulphites, thioglycolates, neutralizing compositions therefor, which contain oxidizing agents, and a variety of other liquid or cream cosmetic compositions, all of which are free from solid particles and which are in the form of solutions or emulsions, i.e. dispersions of liquid droplets in a different liquid medium.

The polymers useful in the present invention are high molecular weight water-soluble quaternary ammonium polymers and copolymers having as the sole constituents of the chain or backbone of the polymer molecule (apart from end groups which terminate each such chain and which has no important effect upon the properties and characteristics of the polymer) units of the following formula:



where R is hydrogen or methyl and wherein A and B are independently (i.e. either both the same or different) alkyl groups having one to twenty-two carbon atoms, lower hydroxyalkyl groups having from one to five carbon atoms, and lower alkyl groups containing terminal amido groups such as betapropionamido; and wherein A and B together with N are piperidinyl or morpholinyl groups. These linear homopolymers and copolymers preferably have a molecular weight of from 20,000 to 3,000,000. In the case of homopolymers, all of the units in the polymer chain are identical, while in the

case of copolymers, the units, while all having the structure defined above, are not all identical to each other. Any of a wide variety of non-toxic or cosmetically acceptable anions, organic as well as inorganic, may be present in the polymer and associated with the quaternary ammonium cationic groups, among which are, for example, acetate, borate, bromide, chloride, citrate, tartrate, bisulphite, bisulphite, sulphate, phosphate, and succinate. Such polymers may be made by polymerizing diallyl dialkyl ammonium chloride or bromide or other appropriate diallyl monomeric ammonium salt using a free radical generating polymerization catalyst such as a peroxide, then using an anion exchange column technique for exchanging the anion, if desired, and are described in U.S. Patents Nos. 3,288,770 and 3,412,019. If a polymer of a chloride is dissolved in an aqueous solution or in a cosmetic base containing salts of any other anions, of course, the resulting solution contains both anions, each being associated to some extent with the quaternary ammonium groups of the polymer. It generally makes no difference, so far as the present invention is concerned, whether the polymer containing a particular desired anion or combination of anions is prepared in pure form before being mixed with a cosmetic base or whether the desired anions are introduced into the cosmetic base in the form of other salts. It is usually most convenient to employ the least expensive salt of the polymer which is readily available, regardless of the anion which it contains, and to add the desired anions in the form of other less expensive salts. Cosmetic bases, as is well known, contain any of a wide variety of non-toxic anions, numerous examples of which are given herein. Particularly preferred is a polymer of a diallyl dimethyl ammonium salt, that is, a polymer having repeating units of the formula given above wherein A and B are both methyl groups, all of the units being identical.

The following Examples are given by way of illustration only.

Example 1

A conventional hair straightening lotion base was prepared having the following composition:

| Ingredient | Weight Percent | |
|------------------------------|----------------|-----|
| Ammonium bisulphite | 10.0 | 110 |
| Urea | 15.0 | |
| Isopropanol | 4.0 | |
| Hydroxyethylcellulose | 1.0 | |
| Ammonium hydroxide to pH 7.1 | | |
| Water to | 100.0 | 115 |

To one portion of the lotion was added 0.5% by weight of a polymer of diallyl

dimethyl ammonium chloride in the form of a 40% by weight aqueous solution having a viscosity of about 12,500 centipoises. Samples of the lotion with and without the added polymer were then employed to treat separate heads of hair under identical conditions, viz. application to clean hair and allowing to stand 20 minutes covered with a turban, application of additional lotion and allowing to stand for another 20 minute period covered with a turban, rinsing with water, applying as neutralizer a 4.5% aqueous solution of sodium sesquicarbonate dihydrate, and finally rinsing with water. It was found that the hair treated with the polymer-containing lotion was soft, lustrous and easy to comb both wet and dry as contrasted to the harsh feeling, difficult-to-comb hair resulting from the other lotion. The difference was still apparent after four weeks and several intervening shampoos. When as little as 0.05% of the polymer or as much as 2.0% were used, the results were very similar.

Similar results were obtained by the process of applying to the hair a 1% by weight solution of the polymer in water as a separate step just before the neutralizer solution in the process of Example 1. The solution was allowed to remain on the hair about five minutes before applying the neutralizer solution.

It has been found that the presence of relatively large quantities of inorganic salts commonly employed in cosmetic bases, such as sodium carbonate, sodium sulphate, sodium phosphate, or sodium tripolyphosphate has little or no effect upon the conditioning properties of a 10% by weight aqueous solution of a polymer of diallyl dimethyl ammonium chloride which has, in the form of a 40% by weight aqueous solution, a viscosity of 5000 cps. Similar results were observed in the case of a 10% solution of a higher molecular weight polymer of the same species which exhibited a viscosity of 130,000 cps. in 40% aqueous solution.

Example 2

Results similar to those obtained in Example 1 were obtained by dissolving 2% by weight of the same polymer in the neutralizer solution instead of mixing polymer with the straightening lotion.

Example 3

A hair waving lotion base was prepared having the following composition:

| | Ingredient | Weight Percent |
|----|--|----------------|
| 60 | Ammonium thioglycolate | 7.8 |
| | Diisopropanolamine | 6.7 |
| | Polyoxyethyleneoxypropylene monostearate | 0.5 |
| | Perfume | 0.125 |
| | Water to | 100.0 |

To one portion of the lotion was added 0.5% by weight of the polymer used in Example 1. Samples of the lotion with and without the added polymer were then employed to treat separate heads of hair under identical conditions, viz. application of the lotion to hair previously shampooed, winding of the hair on curlers, application of additional lotion to the hair and allowing to stand for 15 minutes, rinsing with water and allowing to stand covered with a turban for 30 minutes. A neutralizer consisting of an aqueous solution containing 1.2% hydrogen peroxide and 0.05% of stearyl dimethyl benzyl ammonium chloride was then applied to the hair on the curlers, the hair was removed from the curlers and the neutralizer again applied. The hair waved with the lotion containing the polymer was soft, lustrous, and easy to comb both wet and dry in contrast to the hair waved with the other lotion which was harsh, difficult to comb, and readily tangled. The marked difference in conditioning of surface characteristics of the hair persisted even after both heads had been subjected to six successive shampoos.

Similar results were obtained by dissolving the polymer in the neutralizer instead of in the lotion, as in Example 2, or by applying an aqueous solution of the polymer to the hair as a separate step before neutralizing.

Example 4

A hair bleaching base composition containing the polymer of Example 1 was prepared by mixing 1 volume of composition A and 2 volumes of solution B with 10 volumes of 6% aqueous hydrogen peroxide solution, as follows:

| Composition A | | Weight Percent | 105 |
|------------------------|--|----------------|-----|
| Ingredient | | | |
| Ammonium Persulphate | | 80.0 | |
| Sodium Silicate | | 15.0 | |
| Sodium Lauryl Sulphate | | 5.0 | |
| | | 100.0 | |

| Solution B | | Weight Percent | 110 |
|----------------------------------|--|----------------|-----|
| Ingredient | | | |
| Oleic acid | | 35.0 | |
| Ammonium hydroxide (29%) | | 11.0 | |
| Isopropanol | | 15.0 | |
| Polymer of Example 1 | | 4.0 | |
| Octylphenoxyethoxyethoxy ethanol | | 15.0 | 115 |
| Water | | 20.0 | |
| | | 100.0 | |

The composition was applied to hair and allowed to stand for periods of time from 30 to 90 minutes depending upon the extent of bleaching desired. After rinsing and shampoo-

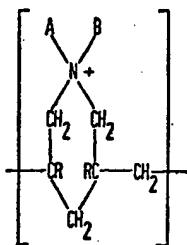
ing the hair displayed the same superior condition as was observed in the hair of the preceding examples, in contrast to the undesirable condition of hair bleached with a similar composition omitting the polymer.

5 **Example 5**
A hair dyeing base composition containing the polymer of Example 1 was prepared by mixing 6% aqueous hydrogen peroxide with 10 an equal volume of the following solution:

| | Ingredient | Weight Percent |
|----|---------------------------------|-------------------|
| | Oleic acid | 20.0 |
| 15 | Ammonium hydroxide (29%) | 7.6 |
| | Octylphenoxyethoxy ethanol | 20.0 |
| | Isopropanol | 18.0 |
| | Polymer of Example 1 | 5.0 |
| 20 | Ethylenediaminetetraacetic acid | 0.05 |
| | Sodium Sulphite | 0.05 |
| | p - Phenylenediamine | 0.1 |
| | Resorcinol | 0.02 |
| | Water to | 100.0 |

25 The composition was applied to the hair, allowed to stand about 20 minutes, rinsed with water and shampooed. The condition of the hair was markedly superior to that of hair treated with the same composition omitting the polymer, the differences being similar to those of the preceding examples.

30 **WHAT WE CLAIM IS:—**
1. A cosmetic composition for application to hair, comprising a cosmetic base (as herein defined) and a high molecular weight water soluble quaternary ammonium polymer having a molecular chain containing units of the formula:



40 wherein R is hydrogen or methyl and A and B are independently alkyl groups having from one to twenty-two carbon atoms, lower hydroxyalkyl groups, or lower alkyl groups containing terminal amido groups, or wherein A and B taken together with N are piperidinyl or morpholinyl groups.

45 2. A composition as claimed in claim 1, in which said cosmetic base contains from

0.5 to 20% by weight of a surface active agent.

3. A composition as claimed in claim 1 or 2, in which A and B are both methyl groups.

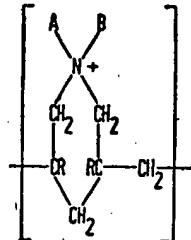
4. A composition as claimed in claim 1 or 2, in which A and B are both ethyl groups.

5. A composition as claimed in any one of claims 1 to 4, in which said cosmetic base is a hair waving or straightening lotion.

6. A composition as claimed in any one of claims 1 to 4, in which said cosmetic base is a hair dye.

7. A cosmetic composition according to claim 1, substantially as herein described in the Examples.

8. A process of changing the surface characteristics of hair, which comprises applying thereto a cosmetic base (as herein defined) and a high molecular weight water soluble quaternary ammonium polymer having a molecular chain containing units of the formula:



70 wherein R is hydrogen or methyl and A and B are independently alkyl groups having from one to twenty-two carbon atoms, lower hydroxyalkyl groups, or lower alkyl groups containing terminal amido groups, or wherein A and B taken together with N are piperidinyl or morpholinyl groups, the cosmetic base and the polymer being applied together or in sequence.

75 9. A package comprising a composition as claimed in any one of claims 1 to 7, together with a propellant liquid in a pressure container.

80 10. A process according to claim 8 substantially as herein described in any of the Examples.

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A. A. THORNTON & CO.,
Chartered Patent Agents,
Northumberland House,
303/306 High Holborn,
London, W.C.1.

Reference has been directed in pursuance of section 9, subsection (1) of the Patents Act 1949, to patents Nos. 1,084,540 and 1,037,028.

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